

RESERVE COPY PATENT SPECIFICATION

6



Convention Date (Germany): Jan. 5, 1932.

Application Date (In United Kingdom): Jan. 5, 1933. No. 415/33.

Complete Accepted: July 5, 1934.

COMPLETE SPECIFICATION.

Improvements in the Vulcanisation of Rubber.

We, I. G. FARBENINDUSTRIE AKTIEN-GESELLSCHAFT, a joint stock company organised under the laws of Germany, of Frankfurt-on-Main, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 This invention relates to improvements in the vulcanisation of rubber.

In accordance with the invention rubber to be vulcanised is incorporated with sulphur and a vulcanisation accelerator not being an amine containing an aliphatic chain having more than 9 carbon atoms but being in admixture with a compound of the latter type, which compound acts as an activator for the accelerator as set out below.

15 In the present specification and claims the term "vulcanisation accelerator" is intended to embrace vulcanisation accelerators other than amines of the type above referred to. It may be mentioned that the latter compounds at least in part possess some accelerating power, they are not, however, true vulcanisation accelerators in a technical sense.

20 The present invention is based on the discovery that the amines in question are capable of activating vulcanisation accelerators quite generally to a far reaching extent without the danger of prevulcanisation occurring. Furthermore, the combined use of vulcanisation accelerators and of the amines defined has the advantage of yielding in many cases vulcanisates of improved tensile strength, even when the total amount of the accelerator + the amine is smaller than the amount in which the respective accelerator is applied in the vulcanisation processes hitherto known.

25 Furthermore, since the amines in question do not discolour the vulcanisates to any substantial degree and do not lend any unpleasant odour to the same, the combined use of vulcanisation accelerators and of amines containing a com-

[Price 1/-]

paratively long aliphatic chain represents a remarkable advance in the art of vulcanising rubber.

As mentioned above, all the known vulcanisation accelerators are activated by the amines in question. The best results are, however, obtained, when applying accelerators not possessing the character of so-called ultra-accelerators, such as unsubstituted or substituted mercaptoarylenethiazoles, thiuram-mono- and disulphides, diarylene-thiazyl-disulphides and the like.

Preferred amines containing an aliphatic chain of more than 9 carbon atoms are for example 2-amino-nono-decane (obtainable by the method described in specification No. 384,314), amino-tridecanes, heptadecylamines, *n*-undecylamine, dodecylamines and so on.

Generally, the amount of the amine to be added may be less than the amount of the accelerator used. Thus, for example, amounts of the amine corresponding to about 0.05 to 0.5% by weight (calculated on the rubber to be vulcanised) will yield good results in most cases.

The term "rubber" as used in the present specification is intended to include natural rubber and also artificial rubber-like masses obtainable by polymerizing in admixture with one another suitable polymerisable compounds, such as butadiene hydrocarbons, styrene, vinylnaphthalenes, acrylic acid, acrylic acid esters, acrylic acid nitriles, unsaturated ketones and the like.

The following examples illustrate the invention.

EXAMPLE 1.

100 parts by weight of first latex crepe,
5 parts by weight of zinc oxide,
3 parts by weight of sulphur,
1 part by weight of stearic acid are well mixed with

0.6 part by weight of dibenzothiazyl-disulphide and

0.3 part by weight of a mixture of 2-amino-nonodecane and ozokerite (60:40) and vulcanised by heating.

Price 4s 6d

Best Available Copy

The following values were obtained:—

	Heating 2 atm. (superatm.)	Tensile strength in kg/sq cm.	extension in %
5	20 minutes	220 S	823
	30 minutes	251	817
	45 minutes	198	753
	60 minutes	198	770
10	3 atm. (superatm.)		
	10 minutes	192	820
	20 minutes	198	777
	30 minutes	198	796
	0.5 atm. (superatm.)		
	40 minutes	insufficiently vulcanised	

S indicates separation of sulphur.

15 For comparison there are given below the values which are obtainable when vulcanising the above mixture with 1 part by weight of di-benzothiazyl disulphide without the addition of 2-amino-nonodecane:—

	Heating 2 atm. (superatmosph.)	Tensile strength in kg/sqcm	Extension in %.
20	20 minutes	112 S	930
	30 minutes	198 S	855
	45 minutes	164	757
	60 minutes	161	738
	3 atm. (superatmosph.)		
25	10 minutes	133 S	885
	20 minutes	171	792
	30 minutes	186	783
	0.5 atm. (superatmosph.)		
30	40 minutes	insufficiently vulcanised	

S indicates separation of sulphur.

EXAMPLE 2.

- 100 parts by weight of raw rubber,
 3 parts by weight of sulphur,
 5 parts by weight of zinc oxide,
 2 parts by weight of stearic acid,
 0.4 part by weight of mercaptobenzothiazole and
 0.1 part by weight of 2-amino-tridecane
 are well mixed and vulcanised by heating.

The following values were obtained:—

	Heating 110° C.	Tensile strength in kg/sqcm	Extension in %.
45	15 minutes	—	—
	20 minutes	28	1025
	3 atm. (superatm.)		
50	15 minutes	208	795
	20 minutes	220	795
	25 minutes	220	805
	30 minutes	190	775
	45 minutes	195	805

Best Available Copy

The following values were obtained when vulcanising the above mixture but without the addition of 2-amino-tridecane:—

Heating 110° C.	Tensile strength in kg/sqcm		Extension in %	
	A	B	A	B
15 minutes	—	—	—	—
20 minutes	—	59	—	1080
3 atm. (superatm.)	—	—	—	—
15 minutes	133 S	143	875	760
20 minutes	149 S	192	856	765
25 minutes	177	183	856	790
30 minutes	160	171	840	780
45 minutes	171	158	850	785

15 A with the addition of 0.4 part by weight of mercapto-benzo-thiazole.

EXAMPLE 3.

A mixture of
100 parts by weight of raw rubber,
3 parts by weight of sulphur,
5 parts by weight of zinc oxide,
0.8 part by weight of dibenzothiazyl
disulphide,

B with the addition of 1.0 part by weight of mercapto-benzo-thiazole.

and
0.2 part by weight of 2-amino-nonodecane.

20 S indicates separation of sulphur.

obtained in the usual manner, is vulcanised by heating.

The following values were obtained compared with those, obtained by vulcanising the above mixture but without the addition of 2-amino-nonodecane:—

Heating 110° C.	Without addition		With addition	
	Tensile strength kg/sqcm	Extension %	Tensile strength kg/sqcm	Extension %
30 minutes	insufficiently vulcanised			
3 atm. (superatm.)	insufficiently vulcanised			
10 minutes	155 S	905	242	845
20 minutes	175	865	198	805
30 minutes	183	885	202	825

S indicates separation of sulphur.

45 The above table shows the considerable increase of the tensile strength by the addition of the small amount of 2-amino-nonodecane. The modulus shows that the vulcanisates obtained with the addition of the 2-amino-nonodecane are essentially tougher.

When working without the addition, a vulcanisate of a tensile strength of 94 kg/sqcm is obtained; from which it results that also in this case a tougher vulcanisate with a greater strength is obtained.

EXAMPLE 4.

EXAMPLE 5.

50 A vulcanisation mixture of
100 parts by weight of raw rubber,
2.5 parts by weight of sulphur,
5 parts by weight of zinc oxide,
0.25 part by weight of tetramethylthiuram disulphide and
0.1 part by weight of 2-amino-nonodecane
60 yields when vulcanised for 20 minutes at 1.5 atmospheres (superatmospheric pressure), a vulcanisate of a tensile strength of 112 kg/sqcm at an extension of 700%.

A mixture of
100 parts by weight of raw rubber,
5 parts by weight of zinc white,
3 parts by weight of sulphur, and
0.8 part by weight of dibenzothiazyl
disulphide
is vulcanised at 3 atmospheres (superatmospheric pressure) for 10, 20 and 30 minutes with and without the addition of 0.2 part by weight of *n*-heptadecylamine. The tensile strengths of the vulcanisates obtained with the addition of the compound in question are by about 40

Best Available Copy

kg/sqcm higher than those of the vulcanizates without the said addition, and the former vulcanisates are also considerably tougher.

5 EXAMPLE 6.

When vulcanising the mixture of example 5 with 2.5 parts by weight of sulphur and 0.25 part by weight of tetramethylthiuram disulphide and with the

addition of a) *n*-undecylamine b) *n*-dodecylamine c) *n*-heptadecylamine the following values were obtained for the tensile strength in kg/sqcm at an extension of 700%, which show that the vulcanisates obtained with the addition of the above named amines are considerably tougher than those obtained without such an addition:—

20	Heating 0.5 atm. (superatm.)	without addition	+0.1 part by weight of a	+0.1 part by weight of b	+0.1 part by weight of c
	30 min. 1.5 atm. (superatm.)				insufficiently vulcanised
25	15 min.	58	88	94	89
	20 min.	81	111	118	114
	30 min.	89	108	113	111

EXAMPLE 7.

A mixed polymerizate is prepared by polymerizing a mixture of 75 parts by weight of butadiene and 25 parts by weight of isopropenylmethyl ketone according to an emulsion-polymerization process. This polymerizate was vulcanized in the following mixture:—
100 parts by weight of the polymerizate
50 parts by weight of carbon black (trade mark "Dixie")
5 parts by weight of zinc white

2 parts by weight of stearic acid
2 parts by weight of a mixture of colophony and pine tar 1:1
1 part by weight of sulphur
0.8 part by weight of accelerator.
As accelerators were applied:
a) 0.8 part by weight of mercaptobenzothiazyl disulphide
b) 0.5 part by weight of mercaptobenzothiazyl disulphide and
0.3 part by weight of 2-aminonodecane.

The following values were obtained:—

55	Heating 3 atm. (superatm.)	Tensile strength in kg/cm ²		Extension %	
		a	b	a	b
	45 min.	160	226	540	440
	60 min.	188	241	350	440
	90 min.	193	249	325	430
	120 min.	143	228	240	385

EXAMPLE 8.

A mixed polymerizate was prepared by polymerizing a mixture of 75 parts by weight of butadiene and 25 parts by weight of acrylic acid nitrile according to an emulsion process. This polymerizate was vulcanized in the following mixture:—
100 parts by weight of polymerizate
60 parts by weight of carbon black (trade mark "Dixie")
10 parts by weight of zinc white

2 parts by weight of stearic acid
2 parts by weight of a mixture of colophony and pine tar 1:1
1 part by weight of sulphur
1 part by weight of accelerator.
As accelerators were applied:—
a) 1 part by weight of mercaptobenzothiazyl disulphide.
b) 0.7 part by weight of mercaptobenzothiazyl disulphide and
0.3 part by weight of 2-amino-nonodecane.

The following figures were obtained:—

85	Heating 3 atm. (superatm.)	Tensile strength in kg/cm ²		Extension %	
		a	b	a	b
	45 min.	191	282	805	710
	60 min.	238	273	690	630
90	90 min.	254	316	710	650
	120 min.	237	306	585	635

Best Available Copy

In the above examples the amines defined may be applied in conjunction with ozokerite, paraffin, paraffin oil or other similar agents.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the vulcanisation of rubber which comprises incorporating with rubber sulphur, a vulcanisation accelerator (as hereinbefore defined) and an amine containing an aliphatic chain having more than 9 carbon atoms, and vulcanising the mixture.

2. Process as claimed in claim 1, in which an accelerator other than an ultra accelerator is used.

3. Process for the vulcanization of rubber substantially as described in the examples.

4. Rubber vulcanisates when produced by the process claimed in any of claims 1—3.

5. For use in the vulcanisation of rubber, a mixture comprising a vulcanisation accelerator (as hereinbefore defined) and an amine containing an aliphatic chain having more than 9 carbon atoms.

Dated the 5th day of January, 1933.

CARPMAELS & RANSFORD,

Agents for Applicants,

24, Southampton Buildings, London, W.C. 2.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1934.

Best Available Copy